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Light-responsive Block Copolymers based on Azobenzene

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Block copolymers (BCs) are of particular interest in the design of novel functional materials based on self-assembling properties. It is well-known that block copolymers can segregated into nanostructures either in bulk or solution. Besides, the incorporation of adequate functional moities in polymeric materials may allow the response of these materials to external stimuli. Furthermore, the response and the self-assemblies properties of BCs can be mutually affected.

On the other hand, light-responsive polymers have received great attention, being azopolymers (containing azobenzene as photochromic units) one of the most investigated, e.g. as optical data storage materials or photomechanical actuators[1]. Azobenzene molecules undergo isomerization between the *trans*and the *cis* states when they are irradiated in their absorption bands. Molecular motions and photoinduced anisotropy may be generated by irradiation using linearly polarized light.

We have previously described the synthesis and characterization of polymethacrylates having cyanoazobenzene as pendant groups, as well as the photoinduced anisotropy and holographic storage in thin films. Nevertheless, thick films are required for volume holography (higher storage capacity). For this last application, BCs can be a good alternative. The block copolymer architecture allows: (1) the confinement of azobenzene into nanodomains, which favors the cooperative motions induced by light, and (2) the dilution of the photochromic units, which allows the processing of thicker films.

We first accomplished the synthesis of linear-linear BCs (Figure 1) containing azobenzene units by ATRP using PMMA-macroninitiators[2]. BCs of high molecular weight have better been approached by a separate ATRP-synthesis of both blocks and coupling by a click reaction.

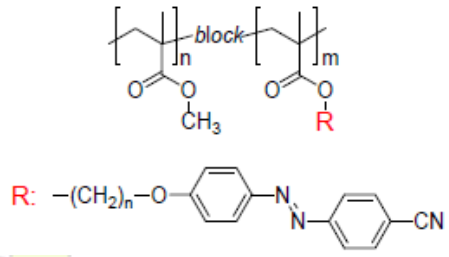

Figure 1. Chemical structure of linear-linear BCs

Synthesis, characterization, morphology and optical properties of films processed from these block copolymers will be discussed and compared with homopolymers.

In order to introduce a precise number of photochromic units, a new kind of azo-BCs were attempted having a linear-dendritic structure (Figure 2).

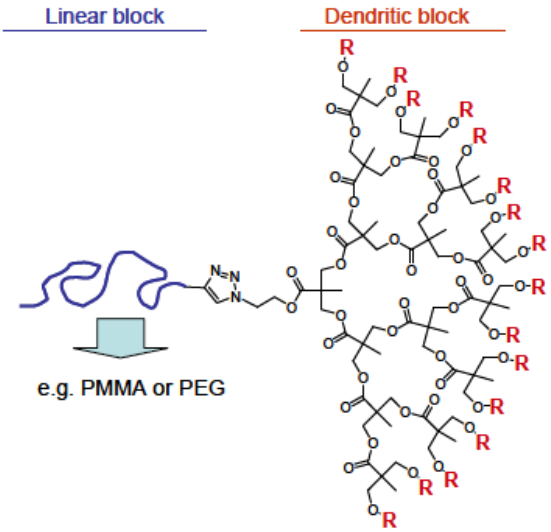

Figure 2.Chemical structure of linear-dendritic BCs.

The click coupling of linear and dendritic blocks (having photochromic units at the periphery) gives rise to different series of BCs[3]. In the case of amphiphilic BCS, self-assembly in aqueous solutions gives rise to different nanoobjects, ranging from nanofibers to vesicles, depending on the generation of the dendritic blocks (Figure 3)[4].

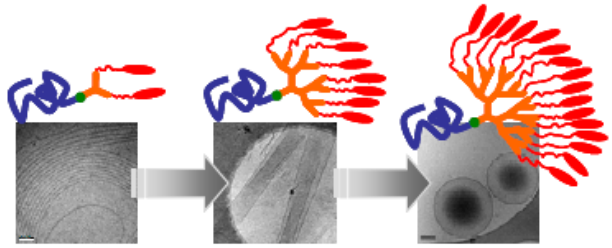

Figure 3.Self-assemblies of linear-dendritic BCs.

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